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ISO/TC 183/WG 6A-DETERMINATION OF ZINC IN ZINC CONCENTRATES STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA 1984-1986

R. Sutarno and W.S. Bowman
Extractive Metallurgy Laboratory

April 1986

(For submission to the Convener of ISO/TC 183/WG 6A , to the Secretariat of ISO/TC 183 and for presentation at the ISO/TC 183 meeting to be held in Sydney, Australia, 1986-04-27 to 1986-05-03)

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Project: 3.0.6.9.02
Analytical Methodology

53pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 86-56 (IR)

MICROMEDIA

ISO/TC 183/WG 6A(WG10-8)
April 1986

ISO/TC 183/WG 6A - DETERMINATION OF ZINC IN ZINC CONCENTRATES STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA 1984-1986

by

R. Sutarno and W.S. Bowman

SUMMARY

The analytical data resulting from the international test on the determination of zinc in zinc concentrates by three titrimetric methods conducted by ISO/TC 183/WG 6A during the period of 1984-1986 have been statistically evaluated. Based on these analytical results, the preliminary estimates of the precision of the analytical method can be expressed in terms of the Zn concentration level by the following equations:

	N8	N9	N11
r	= .0045 X + .1325	= .0067 X -.0223	= -.0029 X + .3788
P	= .0011 X + .2311	= .0173 X -.4248	= -.0078 X + .5759
s_r	= .0016 X + .0468	= .0024 X -.0079	= -.0010 X + .1339
s_L	= -.0013 X + .1097	= .0055 X -.1589	= -.0032 X + .1915

where x is the Zn concentration in the sample (%), r is the repeatability (%), P is the permissible tolerance (%), s_r is the within-laboratory standard deviation (%) and s_L is the between-laboratories standard deviation (%). Three samples with zinc content ranging from 35 to 49 percent were used in this international test. Twelve laboratories participated in this test.

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*Research Scientist and **Technologist, Physical Chemistry Section, Extractive Metallurgy Laboratory, Mineral Sciences Laboratories, CANMET, Energy,Mines and Resources Canada, Ottawa, Ontario K1A 0G1.

ISO/TC 183/WG 6A(WG10-8)
avril 1986

ISO/TC 183/WG 6A - DOSAGE DU ZINC DANS LES CONCENTRÉS DE ZINC ÉVALUATION STATISTIQUE DES DONNÉES DE L'ESSAI INTERNATIONAL 1984-1986

par

R. Sutarno et W.S. Bowman

RÉSUMÉ

Une évaluation statistique a été faite des données analytiques tirées de l'essai international sur le dosage du zinc dans les concentrés de zinc, entrepris selon trois méthodes de titrimétrie par groupe d'étude ISO/TC 183/WG 6A au cours de 1984-1986. Ces résultats analytiques révèlent qu'il est possible d'exprimer la précision de la méthode analytique en fonction de la concentration de zinc à l'aide des équations suivantes:

	N8	N9	N11
r	= 0,0045 x +0,1325	= 0,0067 x -0,0223	= -0.0029 x +0.3788
P	= 0,0011 x +0,2311	= 0,0173 x -0,4248	= -0,0078 x +0,5759
s_r	= 0,0016 x +0,0468	= 0,0024 x -0,0079	= -0,0010 x +0,1339
s_L	= 0,0013 x +0,1097	= 0,0055 x -0,1589	= -0,0032 x +0,1915

où x représente la concentration de Zn dans l'échantillon (%); r, la répétabilité (%); P, la tolérance permise (%); s_r, l'écart-type dans un laboratoire; et s_L, l'écart-type d'un laboratoire à l'autre. Trois échantillons ayant une teneur en zinc qui variait de 35% à 49% ont été utilisés au cours de cet essai international. Douze laboratoires on participé à l'essai.

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*Chercheur et **technologue, Section de la chimie physique, Laboratoire de métallurgie extractive, Laboratoires des sciences minérales; CANMET, Énergie, Mines et Ressources Canada, Ottawa, Ontario K1A 0G1.

INTRODUCTION

The analytical data were collected by the convener of ISO/TC 183/WG 6A (ISO Technical Committee 183 - Copper,Lead and Zinc Ores and Concentrates, Working Group 6A - Zinc in Zinc Concentrates) from an international test conducted during the period of 1984-1986. Three samples of concentrates with zinc contents 35%, 44% and 48.5% were used. Three methods were tested:

(1) Method N8: Determination of zinc in zinc concentrates by complexometric analysis after complete precipitation of interfering elements.

(2) Method N9: Determination of zinc in zinc concentrates by complexometric analysis after selective extraction of zinc.

(3) Method N11: Determination of zinc in zinc concentrates and zinc oxide fumes - Titrimetric solvent extraction method.

Twelve laboratories provided analytical data for methods N8 and N9 and seven laboratories for method N11; each analysed the samples in triplicate.

The purpose of this statistical evaluation is to provide the working group with the preliminary estimates of the precision in the form of repeatability(r), permissible tolerance(P), and within-laboratory(s_r) and between-laboratories(s_L) standard deviations.

PRINCIPLE OF THE ANALYTICAL METHODS

These methods are designed for the accurate determination of zinc in zinc ore concentrates (sulfide, oxides, carbonates, silicates), whether these ores are crude or roasted. The range of application covers zinc contents of 30 to 70%.

(1). Method N8 (Belgian submission)[1]

1.1. Dissolution in Br_2 + HNO_3 mixture for sulfide ores or HNO_3 + H_2S mixture for other ores.

1.2. Precipitation of $Fe(OH)_3$, $Al(OH)_3$ and MnO_2 (the last after oxidation with persulfate ions) in ammoniacal solution.

1.3. Precipitation of Cd, Co, Cu, Ni and Pb as their diethyldithiocarbamate complexes.

1.4. Titration of zinc with ethylenediamine tetraacetic acid (EDTA) solution using xylenol orange indicator, after addition of a buffer solution fixing the pH at 5.8 and of fluoride ions to complex the residual calcium and aluminum.

1.5. Calibration of the EDTA solution by applying the complete method of operation to zinc metal.

(2). Method N9 (Belgian submission)[2]

1. Dissolution on Br_2 + HNO_3 mixture, plus dissolution of any insoluble material in HF + $HClO_4$ (for non-sulfide ores an alternative attack with HNO_3 + H_2SO_4 is possible).

2.2. Selective extraction of the zinc-thiocyanate complex in methylisobutylketone after screening certain elements with thiourea and citrate ions.

Cd is partially extracted but is screened before the final titration. Co, when present, is co-extracted. It must therefore be separated before the selective extraction of the zinc.

2.3. Complexometric titration with EDTA at pH 5.5 using xylenol orange indicator.

2.4. The EDTA solution is standardized against a zinc solution of accurately known content.

(3). Method N11 (Australian submission)[3]

The sample is dissolved in mixed acid and bromine. The zinc thiocyanate complex is extracted into methylisobutylketone. The zinc is re-extracted into aqueous phase and the aqueous phase is titrated with EDTA using a mixed indicator of eriochrome black T and dimethyl yellow.

STATISTICAL EVALUATION

The analytical data collected were statistically evaluated by the procedure described in document ISO/TC 102/TCR 5[4]. Because each participating laboratory analysed only one bottle of each sample, as required by WG Stage A, the two-way analysis of variance (ANOVA) part of the procedure was by-passed. No confirmation of sample homogeneity was made; thus the between-laboratories variance may include the between-bottles variation of the sample. This procedure is illustrated schematically in Figure 1.

The raw data and the detailed calculation are presented in Appendix A. They are summarized in Tables 1 and 2. The raw data are also plotted in Figures 2. The boxed points in these figures signify that the data were suspected to be outliers and were excluded from the estimation of the sample means and precisions. The letter C on the boxed points signifies that the data were suspected to be outliers due to poor precision (Cochran's test) and the letter D due to the deviation from the sample means (Dixon's test). Five percent level of significance was used for both tests.

The estimated precisions (s_r, s_L, r and P) are plotted against their corresponding sample means in Figure 3, and the regression equations of these precisions against sample means were computed and presented in Table 1. Table 2 lists the suspected outliers. Table 3 shows the comparison of sample grand means and precisions obtained by the results of the three methods.

OBSERVATIONS

An ideal standard analytical method is an analytical method that can be applied by any qualified analyst with proper equipment and reagents, with equal precision and accuracy. This implies that, the better the method is standardized, the smaller is the s_L/s_r ratio, and the fewer the number of outliers. The magnitude of the within-laboratory standard deviation itself depends on the state of the art of the method. Experience from another Technical Committee dealing with mineral analyses (iron ores) shows that for a good method, the average s_L/s_r ratio is found to be about 2.

This empirical value has also been confirmed by the s_L/s_r ratio values obtained by the results of international tests conducted by other TC 183 working groups (WG 1A, WG 2A, WG 3A and WG 4A).

Table 1 shows that the within laboratory precision is not as good as expected by the convener (based on his preliminary test). As a result the s_L/s_r ratios seem to be rather low; the reason is that s_L is computed by difference. Table 1a shows that although they are preliminary estimates, the regression equations indicate that there is only a small dependency of the precision on the level of Zn concentration,i.e., the slopes of the regression lines are less than 1%. This is generally considered to be a good sign for major elements. Table 3 shows that the grand means obtained by the three methods tested are virtually identical, and there are no systematic difference in their precisions.

REFERENCES

1. "Accurate determination of zinc in zinc ore concentrates by complexometric analysis after complete precipitation of interfering elements", Belgian submission, ISO/TC 183 N8, 1983-10-18.

2. "Accurate determination of zinc in zinc ore concentrates by complexometric analysis after selective extraction of zinc", Belgian submission, ISO/TC 183 N9, 1983-10-18.

3. "Method for the analysis of zinc concentrates - Part 1 - Determination of the zinc content of zinc concentrates and fumes - Titrimetric solvent extraction method", Australian submission, ISO/TC 183 N11, 1983-10-24.

4. "Procedure for statistical evaluation of analytical data resulting from international tests",ISO/TC 102/TCR 5,1985-06-11.

Table 1

ISO/TC 183/WG 6A Zn in Zn Concentrates

Summary of Precision

El	Meth	Sample	Ko	K	No	N	x	r	P	s_r	s_L	s_L/s_r
Zn	N8	BCR26	12	11	36	33	48.532	.369	.277	.130	.033	.25
Zn	N8	BCR27	12	12	36	36	43.992	.301	.294	.107	.072	.67
Zn	N8	BCR29	12	11	36	33	35.124	.300	.266	.106	.057	.54
Zn	N9	BCR26	12	12	36	36	48.407	.295	.501	.104	.161	1.55
Zn	N9	BCR27	12	9	36	27	44.045	.287	.203	.101	.000	.00
Zn	N9	BCR29	12	11	36	33	35.149	.210	.227	.074	.060	.81
Zn	N11	BCR26	7	6	21	18	48.424	.198	.200	.070	.050	.72
Zn	N11	BCR27	7	7	21	21	43.952	.316	.236	.112	.027	.24
Zn	N11	BCR29	7	7	21	21	35.099	.257	.303	.091	.086	.95

Table 1a

ISO/TC 183/WG 6A Zn in Zn Concentrates

Regression Equations

	N8	N9	N11
r	= .0045 X + .1325	= .0067 X -.0223	= -.0029 X + .3788
P	= .0011 X + .2311	= .0173 X -.4248	= -.0078 X + .5759
s_r	= .0016 X + .0468	= .0024 X -.0079	= -.0010 X + .1339
s_L	= -.0013 X + .1097	= .0055 X -.1589	= -.0032 X + .1915

Table 2

ISO/TC 183/WG 6A-2 Zn in Zn Concentrates

List of outliers

El	Meth	Sample	Cochran (Precision)	Dixon (Accuracy)
Zn	N8	BCR26	-	AU 5
Zn	N8	BCR27	-	-
Zn	N8	BCR29	BE[illegible] 2	-
Zn	N9	BCR26	-	-
Zn	N9	BCR27	-	AU 1
			-	AU 3
			-	JP 1
Zn	N9	BCR29	-	AU 4
Zn	N11	BCR26	JP 2	-
Zn	N11	BCR27	-	-
Zn	N11	BCR29	-	-

Table 3

ISO/TC 183/WG 6A Zn in Zn Concentrates
Comparison between grand means and precisions obtained by methods N8, N9 and N11.

	% Zn			Ratios to N11		
	N8	N9	N11	N8/N11	N9/N11	N11/N11
			Grand mean, x			
BCR26	48.532	48.407	48.424	1.00	1.00	1.00
BCR27	43.992	44.045	43.952	1.00	1.00	1.00
BCR29	35.124	35.149	35.099	1.00	1.00	1.00
			Repeatability, r			
BCR26	.369	.295	.198	1.86	1.49	1.00
BCR27	.301	.287	.316	.95	.91	1.00
BCR29	.300	.210	.257	1.17	.82	1.00
			Permissible tolerance, P			
BCR26	.277	.501	.200	1.38	2.50	1.00
BCR27	.294	.203	.236	1.25	.86	1.00
BCR29	.266	.227	.303	.88	.75	1.00

Abbreviations Used in this Report

s_r = SIGMA-R - within laboratory standard deviation

s_L = SIGMA-L - between laboratories standard deviation

r = R - repeatability

P = permissible tolerance

Ko = total number of participating laboratories

K = number of sets of laboratory results used for ANOVA

No = total number of analytical results

N = number of analytical results used for ANOVA

AU = Australia

BE = BEL = Belgium

FR = France

DE = GER = Germany

JP = Japan

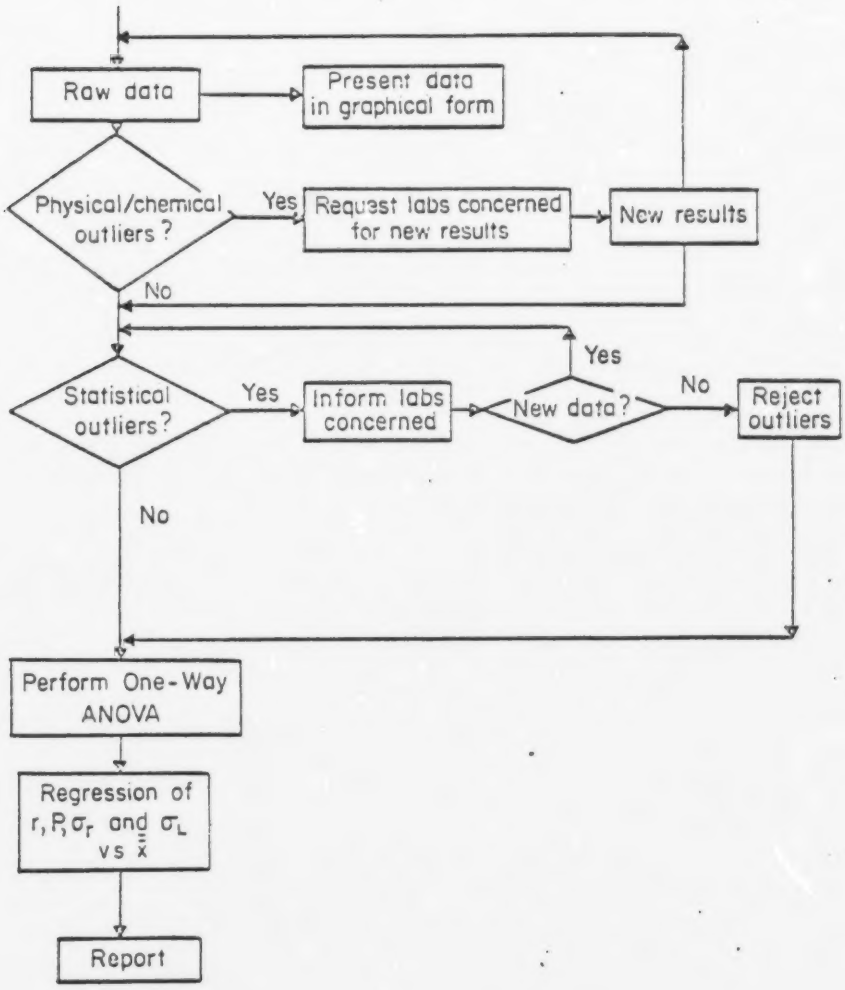

Figure 1. Flow Chart of the Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests.

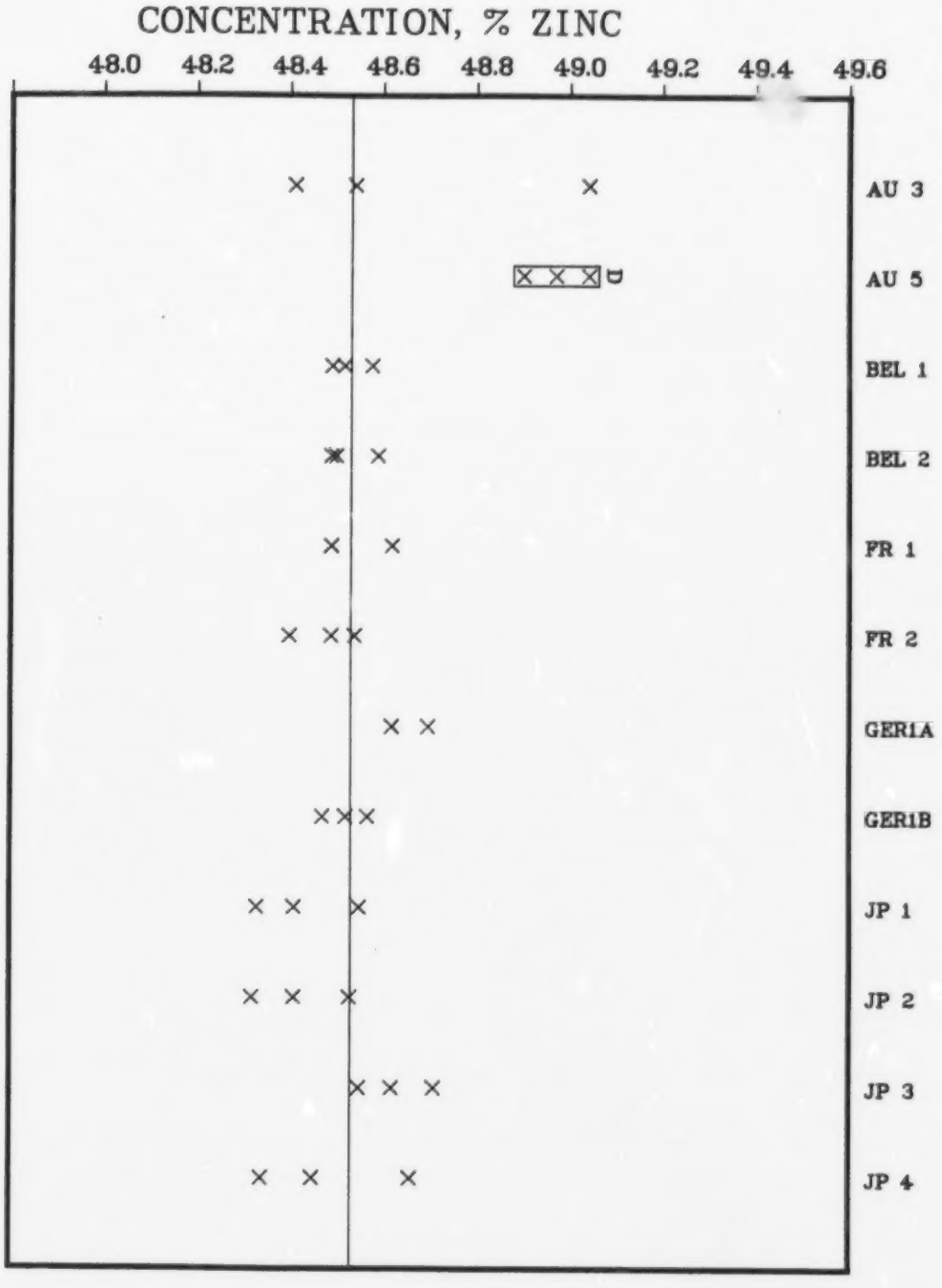

Figure 2.1-N8
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N8 - COMPLEX- PRECIPITATION
SAMPLE: BCR26

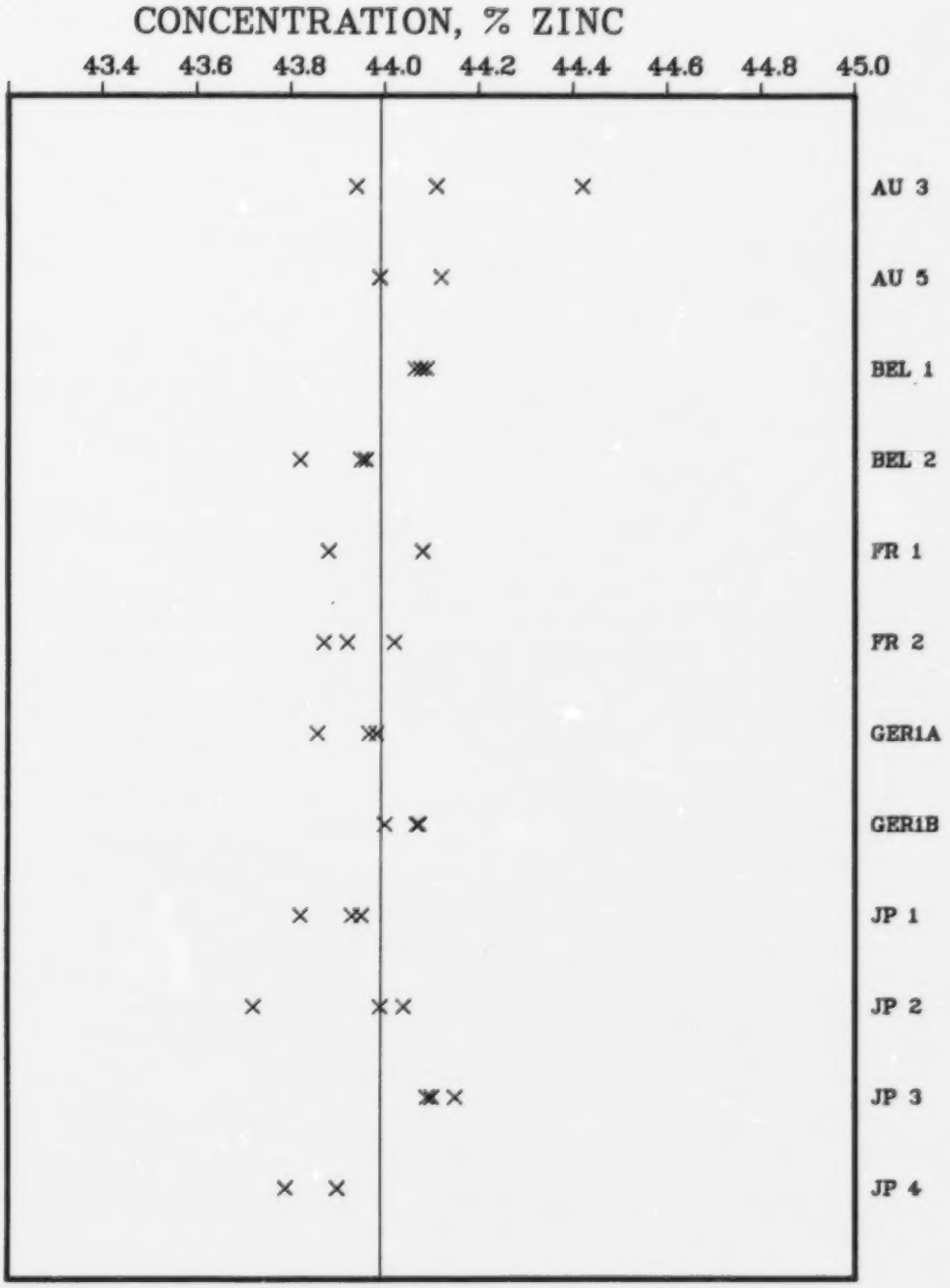

Figure 2.2-N8
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N8 - COMPLEX- PRECIPITATION
SAMPLE: BCR27

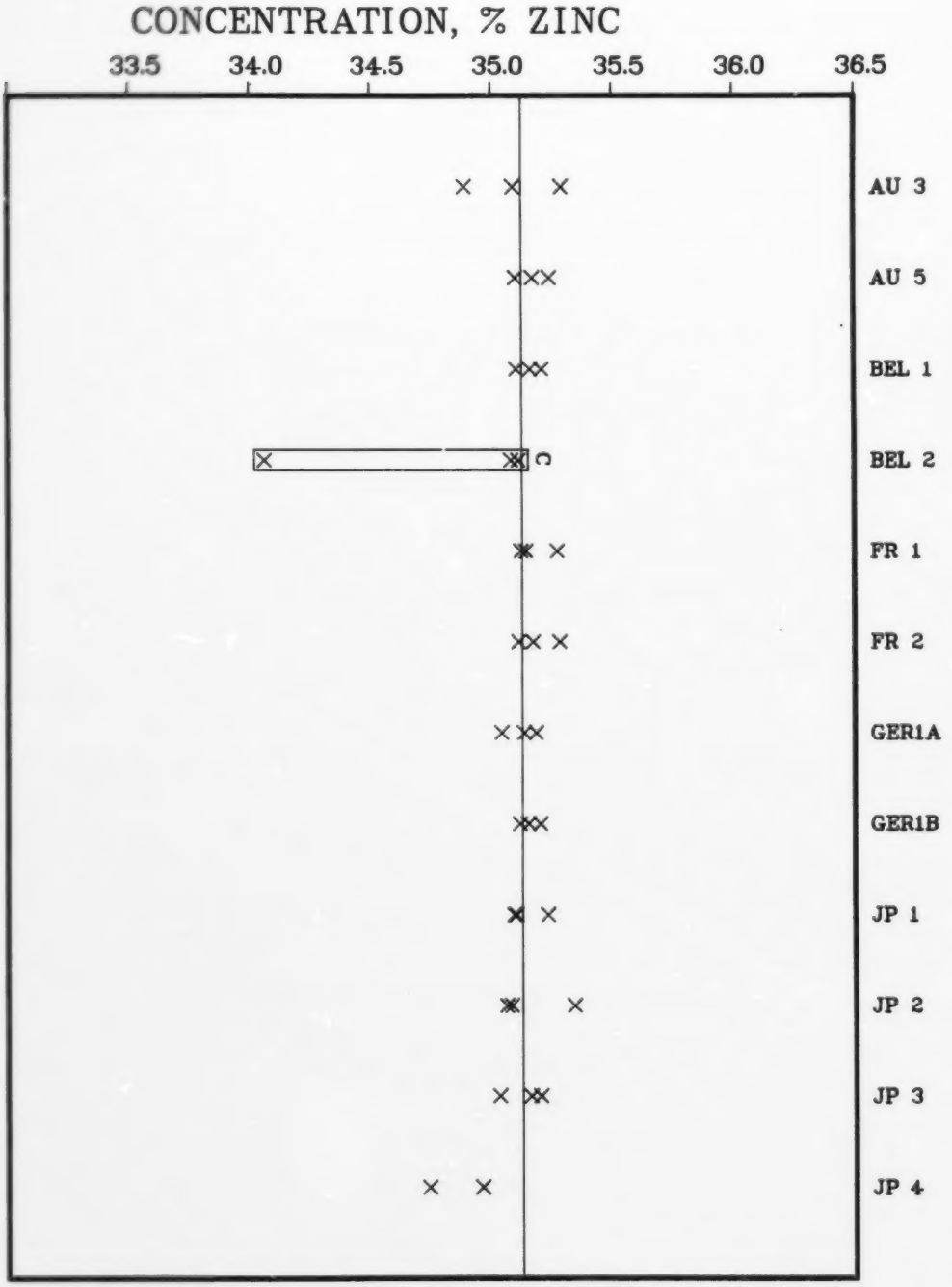

Figure 2.3-N8
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N8 - COMPLEX- PRECIPITATION
SAMPLE: BCR29

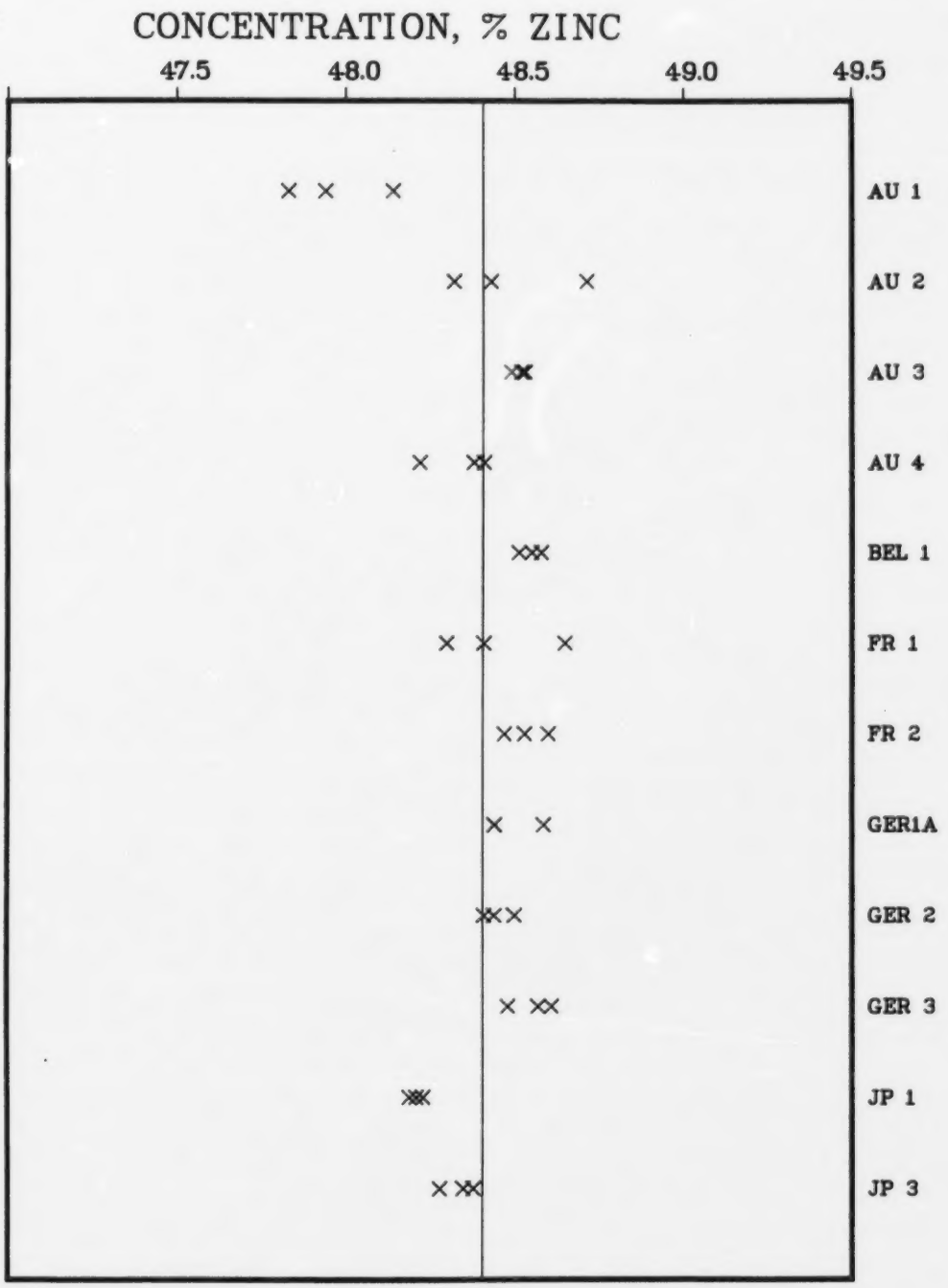

Figure 2.1-N9
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N9 - COMPLEX.- EXTRACTION PH 5
SAMPLE: BCR26

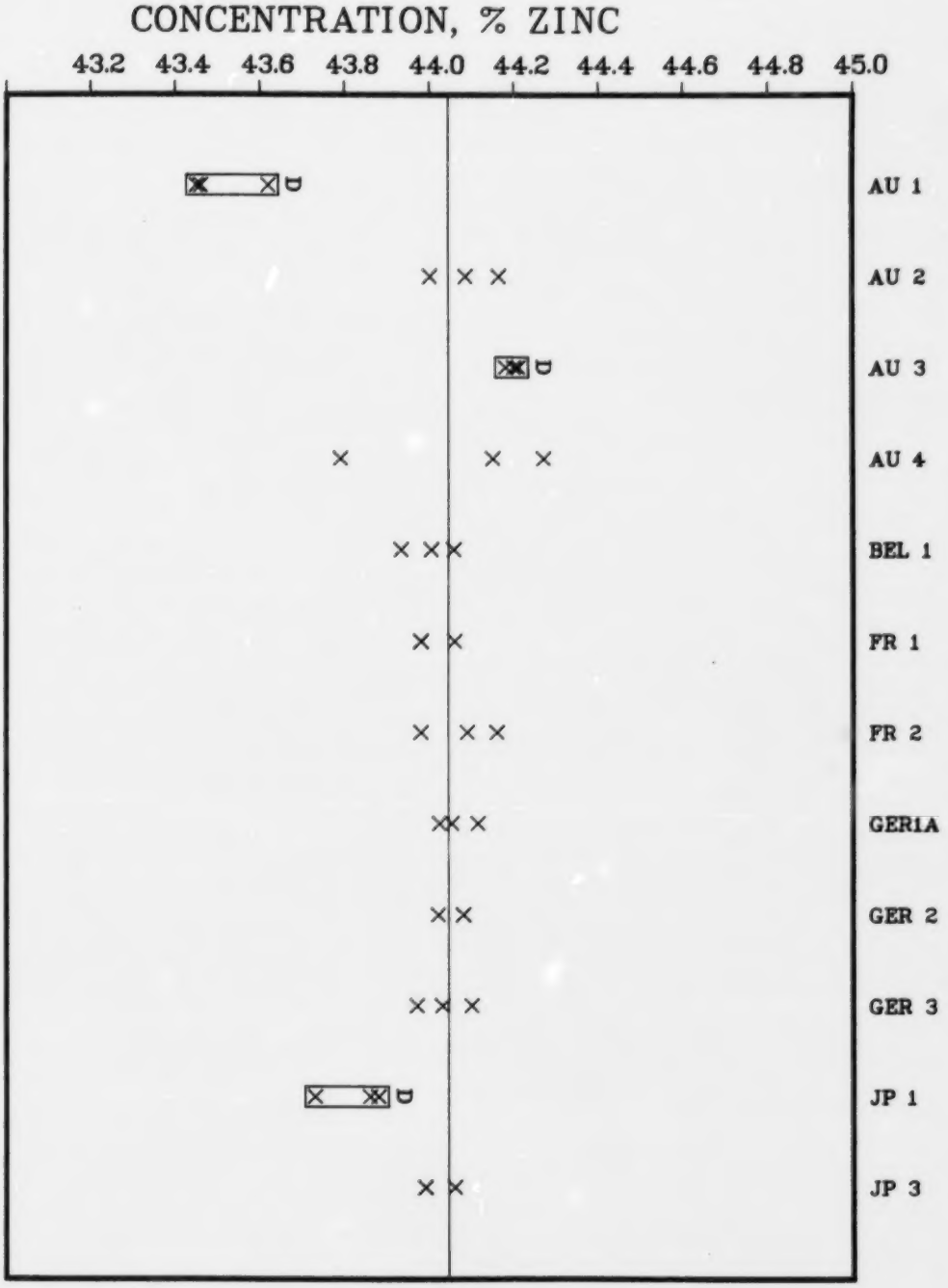

Figure 2.2-N9
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N9 - COMPLEX- EXTRACTION PH 5
SAMPLE: BCR27

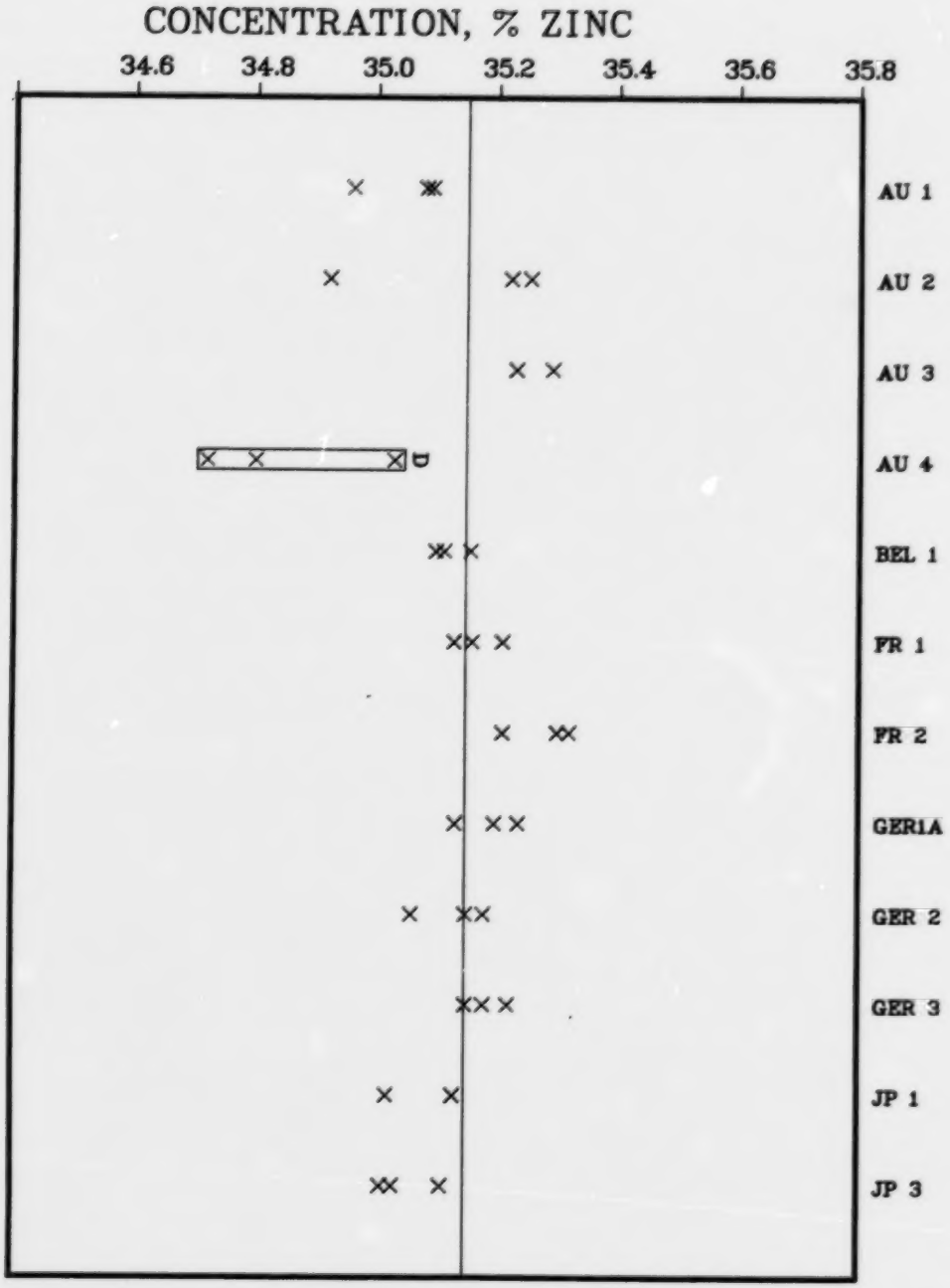

Figure 2.3-N9
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N9 - COMPLEX- EXTRACTION PH 5
SAMPLE: BCR29

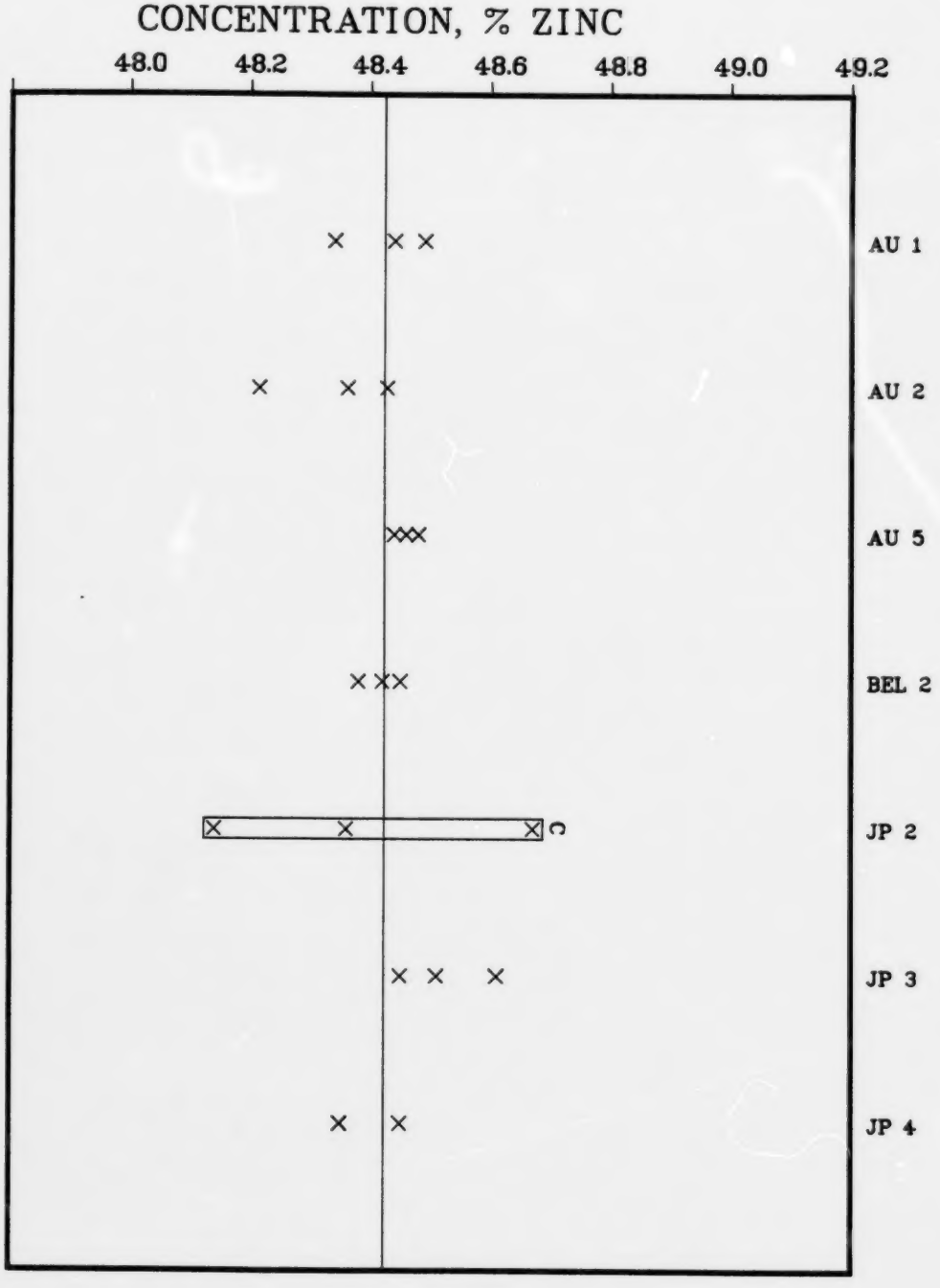

Figure 2.1-N11

ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N11 - COMPLEX- EXTRACTION PH 10

SAMPLE: BCR26

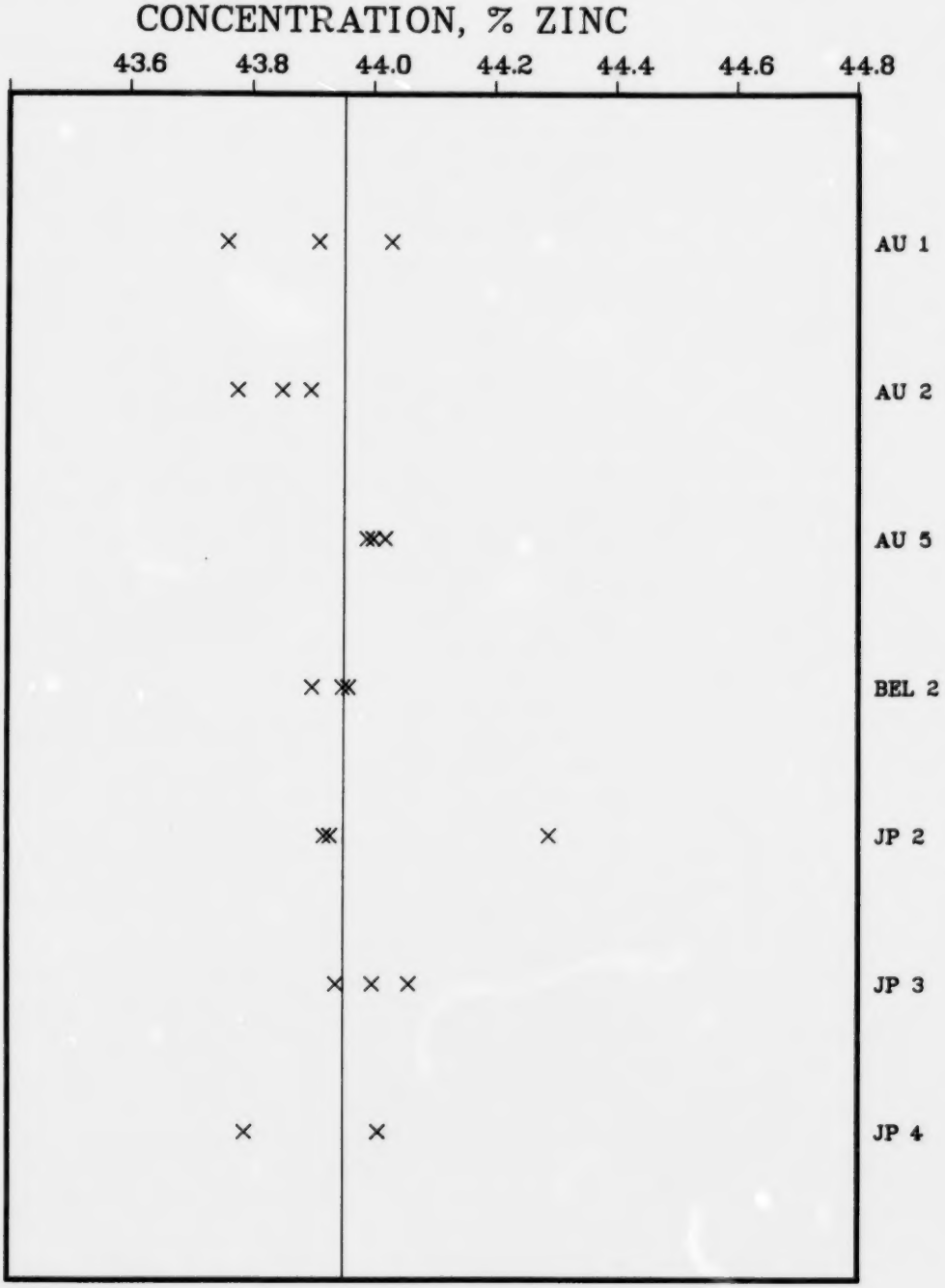

Figure 2.2-N11

ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N11 - COMPLEX- EXTRACTION PH 10

SAMPLE: BCR27

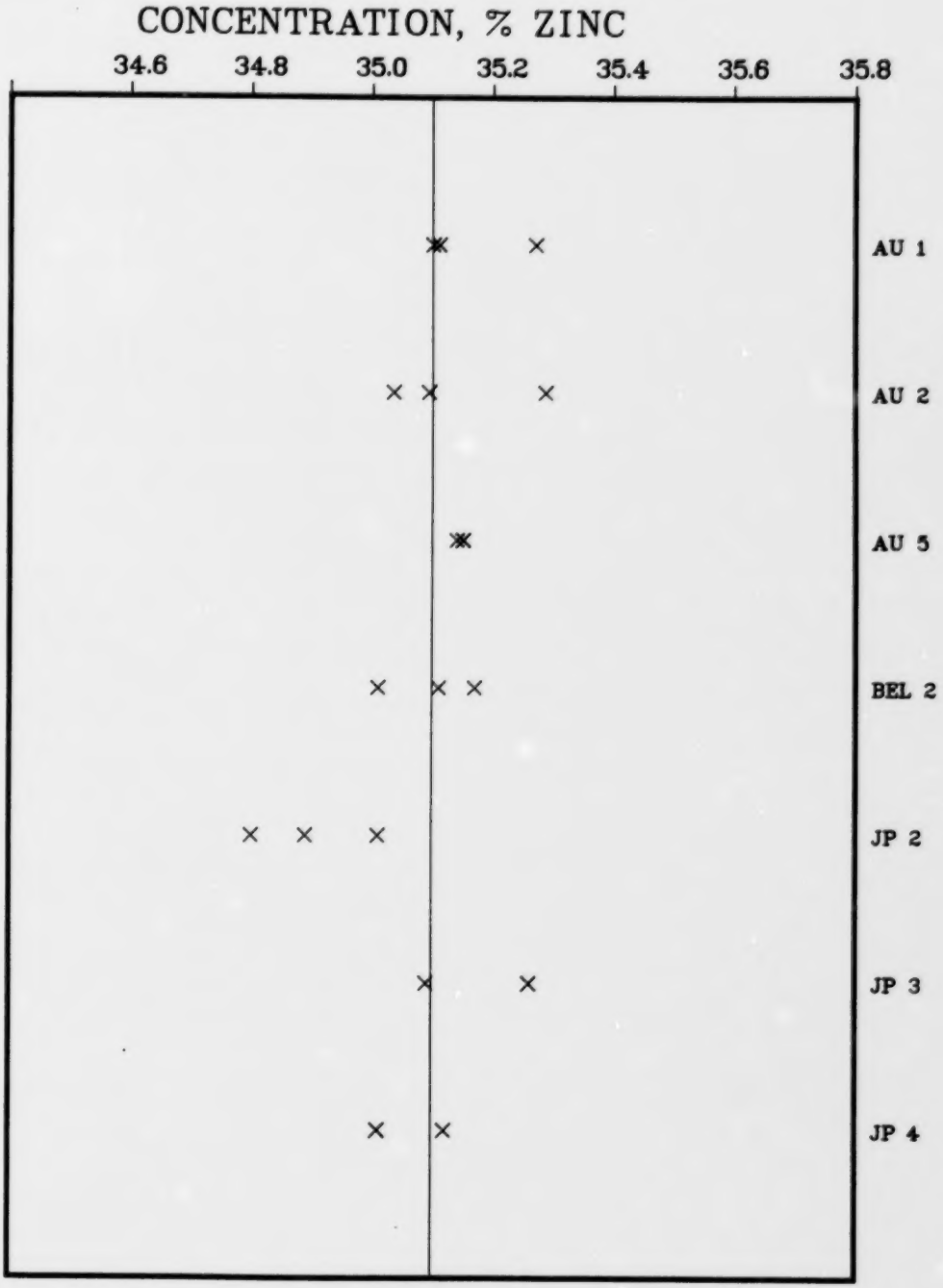

Figure 2.3-N11
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N11 - COMPLEX- EXTRACTION PH 10
SAMPLE: BCR29

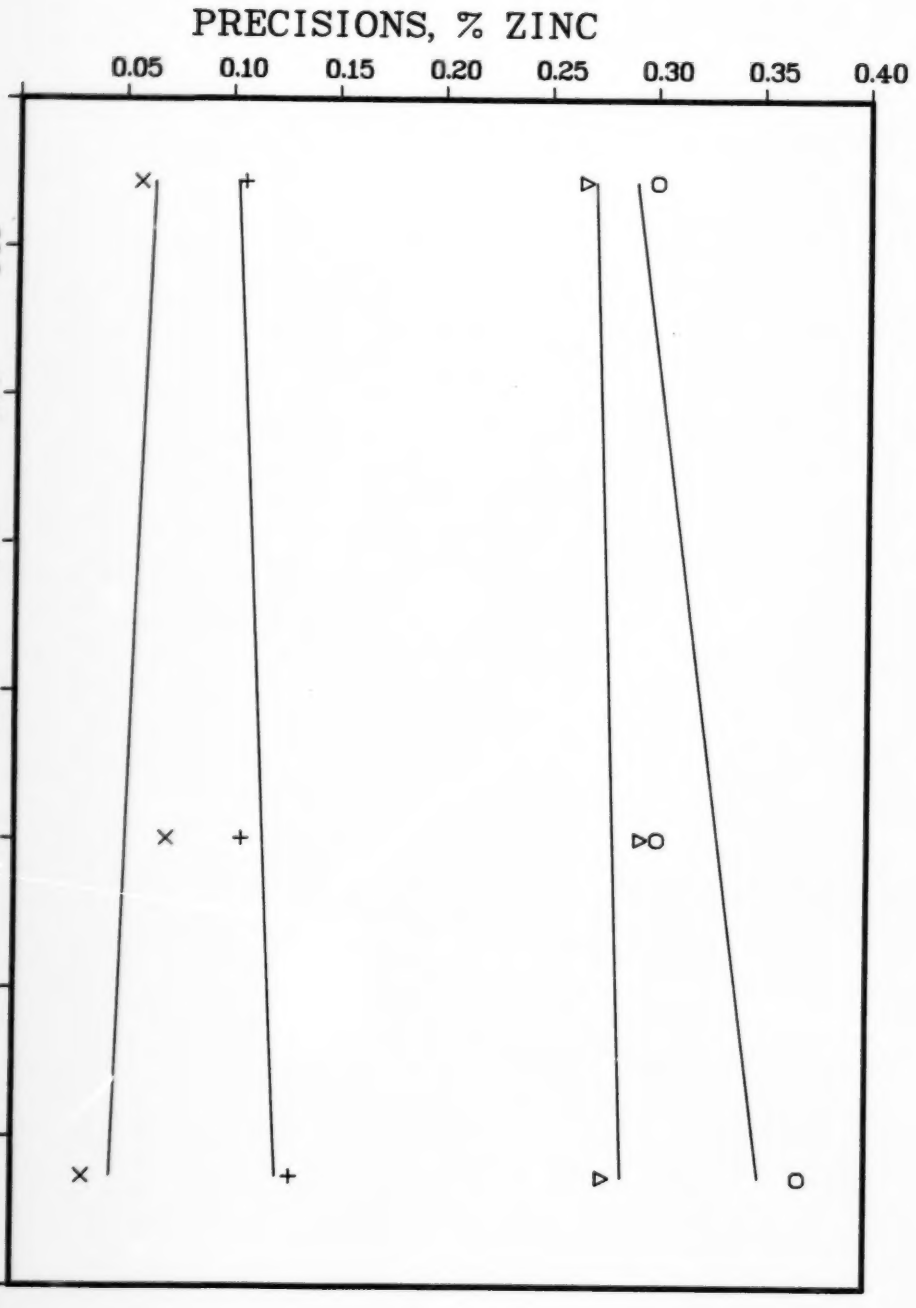

Figure 3-N8
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N8 - COMPLEX- PRECIPITATION

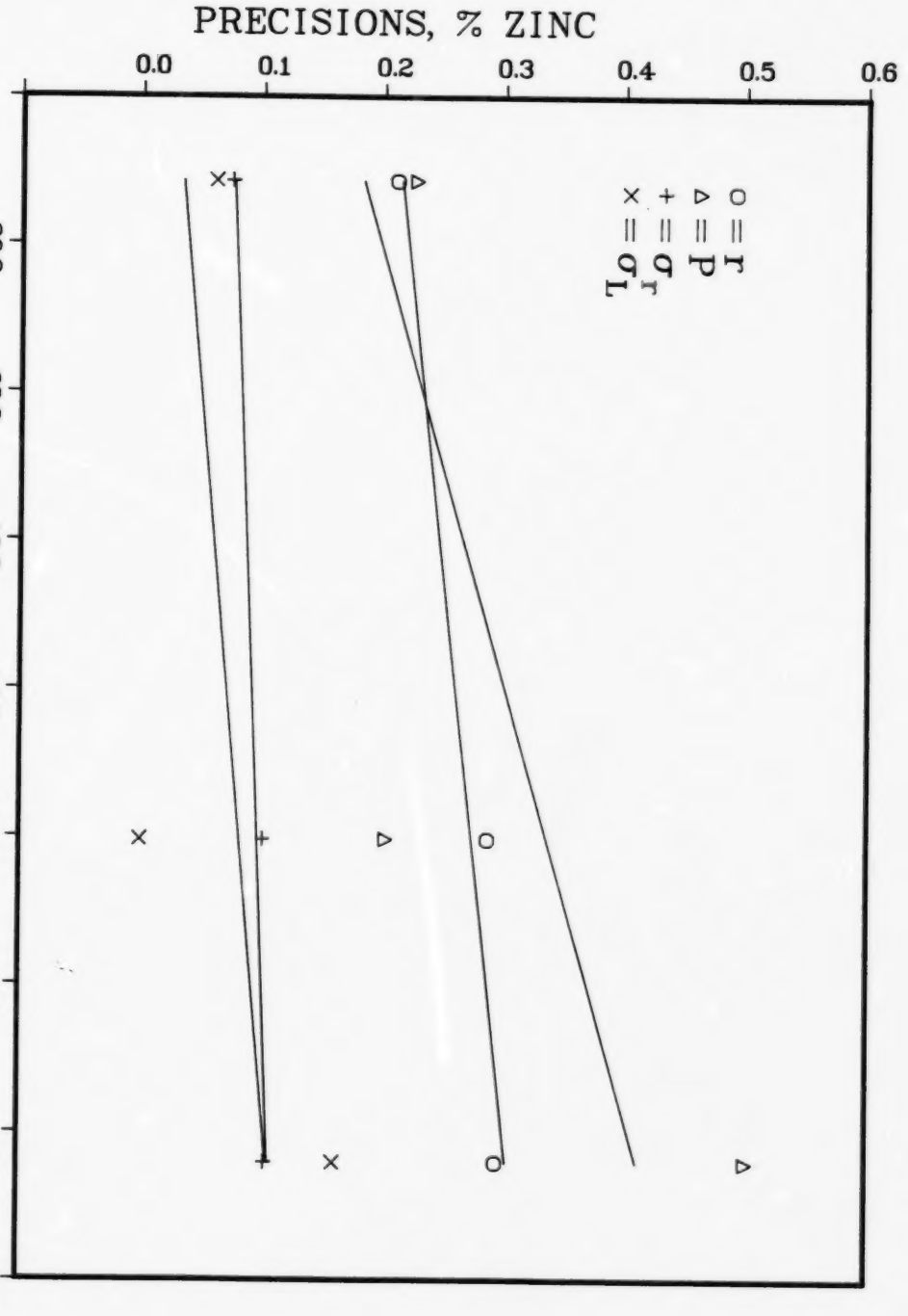

Figure 3-N9

ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N9 - COMPLEX - EXTRACTION PH 5

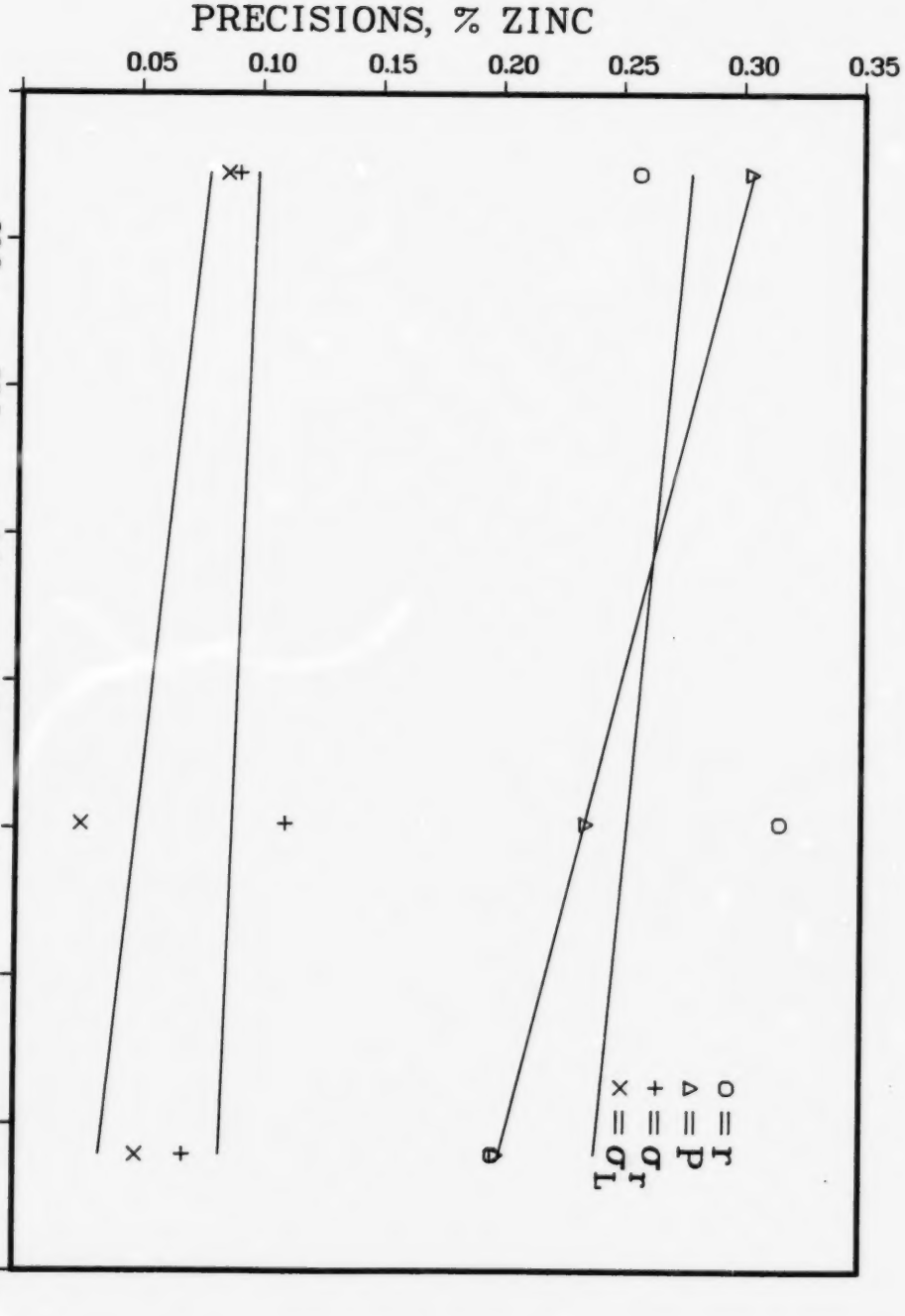

Figure 3-N11
ISO/TC 183/WG 6A-2 ZN IN ZINC CONC. METHOD N11 - COMPLEX - EXTRACTION PH 10

ISO/TC 183/WG 6A-DETERMINATION OF ZINC IN ZINC CONCENTRATES
STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA 1984-1986

APPENDIX A

Detailed Computation of Analytical Data

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR26 BCR 26 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 3	1	48.4100	48.5400	49.0400	48.66333	.1106E+00
2	AU 5	1	48.9000	48.9700	49.0400	48.97000	.4900E-02
3	BE 1	1	48.4910	48.5180	48.5770	48.52867	.1934E-02
4	BE 2	1	48.4900	48.5000	48.5900	48.52667	.3033E-02
5	FR 1	1	48.4900	48.4900	48.6200	48.53333	.5633E-02
6	FR 2	1	48.4000	48.4900	48.5400	48.47667	.5033E-02
7	DE 1A	1	48.6190	48.6200	48.6970	48.64533	.2002E-02
8	DE 1B	1	48.4710	48.5210	48.5680	48.52000	.2353E-02
9	JP 1	1	48.3300	48.4100	48.5500	48.43000	.1240E-01
10	JP 2	1	48.3200	48.4100	48.5300	48.42000	.1110E-01
11	JP 3	1	48.5500	48.6200	48.7100	48.62667	.6433E-02
12	JP 4	1	48.3400	48.4500	48.6600	48.48333	.2643E-01

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR26 BCR 26 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	17.354
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

AU 5 R = .568 D-CRIT(12) = .479

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

AU 5 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR26 BCR 26 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	10	.20285358E+00	.20285358E-01
WITHIN LABS	22	.37397933E+00	.16999061E-01
TOTAL	32	.57683291E+00	

REPEATABILITY VARIANCE	.16999061E-01
REPEATABILITY STD. DEV.	.13038045
BETWEEN-LABORATORIES VARIANCE	.10954323E-02
BETWEEN-LABORATORIES STD. DEV.	.03309732
REPEATABILITY	.36897666
PERMISSIBLE TOLERANCE BETWEEN LABS	.27720948
GRAND MEAN	48.53218182
VARIANCE OF THE GRAND MEAN	.61470781E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR27 BCR 27 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 3	1	43.9400	44.1100	44.4200	44.15667	.5923E-01
2	AU 5	1	43.9900	43.9900	44.1200	44.03333	.5633E-02
3	BE 1	1	44.0640	44.0770	44.0890	44.07667	.1563E-03
4	BE 2	1	43.8200	43.9500	43.9600	43.91000	.6100E-02
5	FR 1	1	43.8800	44.0800	44.0800	44.01333	.1333E-01
6	FR 2	1	43.8700	43.9200	44.0200	43.93667	.5833E-02
7	DE 1A	1	43.8560	43.9660	43.9820	43.93467	.4705E-02
8	DE 1B	1	44.0000	44.0670	44.0720	44.04633	.1616E-02
9	JP 1	1	43.8200	43.9300	43.9500	43.90000	.4900E-02
10	JP 2	1	43.7200	43.9900	44.0400	43.91667	.2963E-01
11	JP 3	1	44.0900	44.1000	44.1500	44.11333	.1033E-02
12	JP 4	1	43.7900	43.9000	43.9000	43.86333	.4033E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR27 BCR 27 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	17.959
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR27 BCR 27 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	11	.29366208E+00	.26696553E-01
WITHIN LABS	24	.27242267E+00	.11350944E-01
TOTAL	35	.56608475E+00	

REPEATABILITY VARIANCE	.11350944E-01
REPEATABILITY STD. DEV.	.10654081
BETWEEN-LABORATORIES VARIANCE	.51152028E-02
BETWEEN-LABORATORIES STD. DEV.	.07152065
REPEATABILITY	.30151050
PERMISSIBLE TOLERANCE BETWEEN LABS	.29397523
GRAND MEAN	43.99175000
VARIANCE OF THE GRAND MEAN	.74157092E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR29 BCR 29 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 3	1	34.8900	35.0900	35.2900	35.09000	.4000E-01
2	AU 5	1	35.1000	35.1700	35.2400	35.17000	.4900E-02
3	BE 1	1	35.1020	35.1590	35.2070	35.15600	.2763E-02
4	BE 2	1	34.0600	35.0800	35.1100	34.75000	.3573E+00
5	FR 1	1	35.1200	35.1400	35.2700	35.17667	.6633E-02
6	FR 2	1	35.1100	35.1700	35.2800	35.18667	.7433E-02
7	DE 1A	1	35.0390	35.1320	35.1820	35.11767	.5266E-02
8	DE 1B	1	35.1140	35.1500	35.1990	35.15433	.1820E-02
9	JP 1	1	35.0900	35.1000	35.2300	35.14000	.6100E-02
10	JP 2	1	35.0600	35.0800	35.3400	35.16000	.2440E-01
11	JP 3	1	35.0300	35.1600	35.2000	35.13000	.7900E-02
12	JP 4	1	34.7400	34.9600	34.9600	34.88667	.1613E-01

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR29 BCR 29 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	27.277
CHI-SQUARE(.95,11)	19.681

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

BE 2 C-CALC = .743 C-CRIT(3,12) = .392

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

BE 2 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N8 - PRECIPITATION
SAMPLE: BCR29 BCR 29 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	10	.20961230E+00	.20961230E-01
WITHIN LABS	22	.24669933E+00	.11213606E-01
TOTAL	32	.45631164E+00	

REPEATABILITY VARIANCE	.11213606E-01
REPEATABILITY STD. DEV.	.10589432
BETWEEN-LABORATORIES VARIANCE	.32492081E-02
BETWEEN-LABORATORIES STD. DEV.	.05700183
REPEATABILITY	.29968091
PERMISSIBLE TOLERANCE BETWEEN LABS	.26632106
GRAND MEAN	35.12436364
VARIANCE OF THE GRAND MEAN	.63518880E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR26 BCR 26 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	47.8300	47.9400	48.1400	47.97000	.2470E-01
2	AU 2	1	48.3210	48.4300	48.7130	48.48800	.4094E-01
3	AU 3	1	48.4900	48.5200	48.5300	48.51333	.4333E-03
4	AU 4	1	48.2200	48.3800	48.4100	48.33667	.1043E-01
5	BE 1	1	48.5130	48.5510	48.5790	48.54767	.1097E-02
6	FR 1	1	48.3000	48.4100	48.6500	48.45333	.3203E-01
7	FR 2	1	48.4700	48.5300	48.6000	48.53333	.4233E-02
8	DE 1A	1	48.4400	48.4410	48.5860	48.48900	.7057E-02
9	DE 2	1	48.4100	48.4400	48.5000	48.45000	.2100E-02
10	DE 3	1	48.4800	48.5700	48.6100	48.55333	.4433E-02
11	JP 1	1	48.1900	48.2100	48.2300	48.21000	.4000E-03
12	JP 3	1	48.2800	48.3500	48.3800	48.33667	.2633E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR26 BCR 26 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	18.584
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR26 BCR 26 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	11	.97625756E+00	.88750687E-01
WITHIN LABS	24	.26098667E+00	.10874444E-01
TOTAL	35	.12372442E+01	

REPEATABILITY VARIANCE	.10874444E-01
REPEATABILITY STD. DEV.	.10428060
BETWEEN-LABORATORIES VARIANCE	.25958747E-01
BETWEEN-LABORATORIES STD. DEV.	.16111719
REPEATABILITY	.29511411
PERMISSIBLE TOLERANCE BETWEEN LABS	.50144509
GRAND MEAN	48.40677778
VARIANCE OF THE GRAND MEAN	.24652969E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR27 BCR 27 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	43.4500	43.4600	43.6200	43.51000	.9100E-02
2	AU 2	1	44.0010	44.0860	44.1640	44.08367	.6646E-02
3	AU 3	1	44.1800	44.2000	44.2100	44.19667	.2333E-03
4	AU 4	1	43.7900	44.1500	44.2700	44.07000	.6240E-01
5	BE 1	1	43.9330	44.0040	44.0580	43.99833	.3930E-02
6	FR 1	1	43.9800	43.9800	44.0600	44.00667	.2133E-02
7	FR 2	1	43.9800	44.0900	44.1600	44.07667	.8233E-02
8	DE 1A	1	44.0230	44.0530	44.1150	44.06367	.2201E-02
9	DE 2	1	44.0200	44.0800	44.0800	44.06000	.1200E-02
10	DE 3	1	43.9700	44.0300	44.1000	44.03333	.4233E-02
11	JP 1	1	43.7300	43.8600	43.8800	43.82333	.6633E-02
12	JP 3	1	43.9900	43.9900	44.0600	44.01333	.1633E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR27 BCR 27 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	17.989
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

AU 1	R =	.546	D-CRIT(12) =	.479
AU 3	R =	.570	D-CRIT(11) =	.502
JP 1	R =	.691	D-CRIT(10) =	.530

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

AU 1	DIXON'S TEST FOR LABORATORY MEANS
AU 3	DIXON'S TEST FOR LABORATORY MEANS
JP 1	DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR27 BCR 27 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	8	.25447185E-01	.31808981E-02
WITHIN LABS	18	.18522267E+00	.10290148E-01
TOTAL	26	.21066985E+00	

REPEATABILITY VARIANCE	.10290148E-01
REPEATABILITY STD. DEV.	.10144037
BETWEEN-LABORATORIES VARIANCE	.00000000E+00
BETWEEN-LABORATORIES STD. DEV.	.00000000
REPEATABILITY	.28707624
PERMISSIBLE TOLERANCE BETWEEN LABS	.20299356
GRAND MEAN	44.04507407
VARIANCE OF THE GRAND MEAN	.38111660E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR29 BCR 29 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	34.9600	35.0800	35.0900	35.04333	.5233E-02
2	AU 2	1	34.9210	35.2210	35.2530	35.13167	.3354E-01
3	AU 3	1	35.2300	35.2300	35.2900	35.25000	.1200E-02
4	AU 4	1	34.7200	34.8000	35.0300	34.85000	.2590E-01
5	BE 1	1	35.0990	35.1130	35.1570	35.12300	.9160E-03
6	FR 1	1	35.1300	35.1600	35.2100	35.16667	.1633E-02
7	FR 2	1	35.2100	35.3000	35.3200	35.27667	.3433E-02
8	DE 1A	1	35.1320	35.1970	35.2360	35.18833	.2760E-02
9	DE 2	1	35.0600	35.1500	35.1800	35.13000	.3900E-02
10	DE 3	1	35.1500	35.1800	35.2200	35.18333	.1233E-02
11	JP 1	1	35.0200	35.1300	35.1300	35.09333	.4033E-02
12	JP 3	1	35.0100	35.0300	35.1100	35.05000	.2800E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR29 BCR 29 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	14.338
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

AU 4 R = .483 D-CRIT(12) = .479

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

AU 4 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N9 - EXTRACT. PH 5
SAMPLE: BCR29 BCR 29 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	10	.16481939E+00	.16481939E-01
WITHIN LABS	22	.12136867E+00	.55167576E-02
TOTAL	32	.28618806E+00	

REPEATABILITY VARIANCE	.55167576E-02
REPEATABILITY STD. DEV.	.07427488
BETWEEN-LABORATORIES VARIANCE	.36550606E-02
BETWEEN-LABORATORIES STD. DEV.	.06045710
REPEATABILITY	.21019791
PERMISSIBLE TOLERANCE BETWEEN LABS	.22663758
GRAND MEAN	35.14875758
VARIANCE OF THE GRAND MEAN	.49945271E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR26 BCR 26 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	48.3400	48.4400	48.4900	48.42333	.5833E-02
2	AU 2	1	48.2140	48.3620	48.4280	48.33467	.1201E-01
3	AU 5	1	48.4400	48.4600	48.4800	48.46000	.4000E-03
4	BE 2	1	48.3800	48.4200	48.4500	48.41667	.1233E-02
5	JP 2	1	48.1400	48.3600	48.6700	48.39000	.7090E-01
6	JP 3	1	48.4500	48.5100	48.6100	48.52333	.6533E-02
7	JP 4	1	48.3500	48.3500	48.4500	48.38333	.3333E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR26 BCR 26 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	13.015
CHI-SQUARE(.95, 6)	12.596

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

JP 2 C-CALC = .707 C-CRIT(3, 7) = .561

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

JP 2 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR26 BCR 26 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	5	.62551111E-01	.12510222E-01
WITHIN LABS	12	.58685333E-01	.48904444E-02
TOTAL	17	.12123644E+00	

REPEATABILITY VARIANCE	.48904444E-02
REPEATABILITY STD. DEV.	.06993171
BETWEEN-LABORATORIES VARIANCE	.25399259E-02
BETWEEN-LABORATORIES STD. DEV.	.05039768
REPEATABILITY	.19790675
PERMISSIBLE TOLERANCE BETWEEN LABS	.19981380
GRAND MEAN	48.42355556
VARIANCE OF THE GRAND MEAN	.69501234E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR27 BCR 27 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	43.7600	43.9100	44.0300	43.90000	.1830E-01
2	AU 2	1	43.7770	43.8500	43.8970	43.84133	.3656E-02
3	AU 5	1	43.9900	44.0000	44.0200	44.00333	.2333E-03
4	BE 2	1	43.9000	43.9500	43.9600	43.93667	.1033E-02
5	JP 2	1	43.9200	43.9300	44.2900	44.04667	.4443E-01
6	JP 3	1	43.9400	44.0000	44.0600	44.00000	.3600E-02
7	JP 4	1	43.7900	44.0100	44.0100	43.93667	.1613E-01

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR27 BCR 27 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	11.818
CHI-SQUARE(.95, 6)	12.596

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR27 BCR 27 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	6	.87966476E-01	.14661079E-01
WITHIN LABS	14	.17477933E+00	.12484238E-01
TOTAL	20	.26274581E+00	

REPEATABILITY VARIANCE	.12484238E-01
REPEATABILITY STD. DEV.	.11173289
BETWEEN-LABORATORIES VARIANCE	.72561375E-03
BETWEEN-LABORATORIES STD. DEV.	.02693722
REPEATABILITY	.31620407
PERMISSIBLE TOLERANCE BETWEEN LABS	.23622844
GRAND MEAN	43.95209524
VARIANCE OF THE GRAND MEAN	.69814664E-03

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR29 BCR 29 ZINC WT %

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS ZINC			LAB MEAN	LAB VARIANCE
1	AU 1	1	35.1000	35.1100	35.2700	35.16000	.9100E-02
2	AU 2	1	35.0350	35.0930	35.2860	35.13800	.1727E-01
3	AU 5	1	35.1400	35.1500	35.1500	35.14667	.3333E-04
4	BE 2	1	35.0100	35.1100	35.1700	35.09667	.6533E-02
5	JP 2	1	34.8000	34.8900	35.0100	34.90000	.1110E-01
6	JP 3	1	35.0900	35.2600	35.2600	35.20333	.9633E-02
7	JP 4	1	35.0100	35.0100	35.1200	35.04667	.4033E-02

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR29 BCR 29 ZINC WT %

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	8.679
CHI-SQUARE(.95, 6)	12.596

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 6A/WG 6A-2 --- ZINC IN ZINC CONC. METHOD N11 - EXTRACT. PH 10
SAMPLE: BCR29 BCR 29 ZINC WT %

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	6	.18223314E+00	.30372191E-01
WITHIN LABS	14	.11540467E+00	.82431905E-02
TOTAL	20	.29763781E+00	

REPEATABILITY VARIANCE	.82431905E-02
REPEATABILITY STD. DEV.	.09079202
BETWEEN-LABORATORIES VARIANCE	.73763333E-02
BETWEEN-LABORATORIES STD. DEV.	.08588558
REPEATABILITY	.25694141
PERMISSIBLE TOLERANCE BETWEEN LABS	.30345636
GRAND MEAN	35.09876190
VARIANCE OF THE GRAND MEAN	.14462948E-02